LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-CONF-443431

New Detector Materials for International Safeguards

A. D. Dougan, S. Payne

July 19, 2010

Institute of Nuclear Materials Management
Baltimore, MD, United States
July 11, 2010 through July 15, 2010

LLNL-CONF-443431

NEW DETECTOR MATERIALS FOR INTERNATIONAL SAFEGUARDS

Arden Dougan and Steve Payne
Lawrence Livermore National Laboratory
P.O. Box 808, Livermore, CA 94551

ABSTRACT

In July 2009, the Department of Energy Office of Dismantlement and Transparency sponsored a Workshop at LLNL by entitled, "Advanced Radiation Detection Materials for Safeguards NDA". The goals of the workshop were to bring together experts on materials research, radiation detection and safeguards; to better understand the needs for new radiation detector materials for Next Generation Safeguards; and to identify the research required to introduce these new materials into commercial-off-the-shelf detectors. The Workshop was focused on materials that have not yet been implemented for gamma or neutron detectors to address challenges in safeguards. For gamma detectors, we discussed possible routes to a portable in-field gamma detector that might be employed in a Complementary Access Inspection as well as detectors that could be used to measure enrichment. Many neutron detectors were proposed as substitutes for helium-3 detectors. These new neutron detectors might be used for multiplicity counters, or to measure neutron energy or spent fuel. We discussed detector material prospects for harsh environments such as acid or salt baths, high temperatures, cold and humid environments, or high radiation fields. In this paper we will recount many of the topics of this workshop.

APPLICATIONS IDENTIFIED

The goal of the Next Generation Safeguards Initiative is to strengthen international safeguards through the development and application of tools, technologies, and methods to optimize the effectiveness and efficiency of safeguards at both the facility and state levels. The three objectives are: (1)

- **Objective 4.1:** Develop advanced tools and methods to detect diversion of declared nuclear materials.
- **Objective 4.2:** Develop advanced tools and methods to detect undeclared production or processing of nuclear material.
- **Objective 4.3:** Provide information analysis solutions to improve state level assessments.

Toward this end, several applications were identified. Applications identified included detectors for portable in-field use, enrichment measurements, alternatives to helium-3, and harsh environments. In this section we describe the uses of each type of detector in more detail and the requirements for an "ideal" detector.

Portable In-field Gamma Detectors

Portable in-field gamma detectors can be used to support inspectors making measurements inside or outside of facilities. These measurements detect, identify, quantify, and resolve key ratios (for Pu and HEU). They may be for Complementary Access inspection and/or to discover undeclared activities, such as in a Limited Frequency Unannounced Access, or LFUA. Detectors are also needed to measure trace materials on a swipe (an alpha-beta detector may be useful, but outside the scope of this study). Requirements for these detectors include the need to measure plutonium and uranium isotopics at high resolution/precision. Accurate uranium isotopic measurements demand 0.5% resolution at 100 keV, while plutonium isotopics to be better than 1% at 100 keV. The measurements nominally take between

5-10 minutes to acquire adequate statistics. The count rate is on the order of 10^5-10^6 gammas/second for Pu and 10^4-10^5 γ/sec for U, unshielded (assuming volumetric measurements without self-shielding). The energy range for these detectors is from 50 keV to 200 keV for U and 50 keV to 1 MeV for Pu.
The detectors will need to be rugged, lightweight and typically work in temperature ranges between -40 to 40 ^{0}C. The detectors need to be readily transportable by airplane. Ideally, detectors would not utilize a small radioactive source for internal calibrations to simplify transport. The detector should not require any consumables such as liquid nitrogen. An additional option would be to incorporate tamper-indicating features.

Current detectors used for portable in-field measurements are high purity germanium and sodium iodide detectors, which are used for enrichment (see next section). In general, the existing detectors need to be smaller in size and be handheld. The cryocooled high purity germanium (HPGe) detectors are available commercially but have weaknesses in ruggedness and battery life. A new HPGe detector under development is shown in Figure 1, for which the weight is reduce by >2x compared to commercially available equipment. (2)

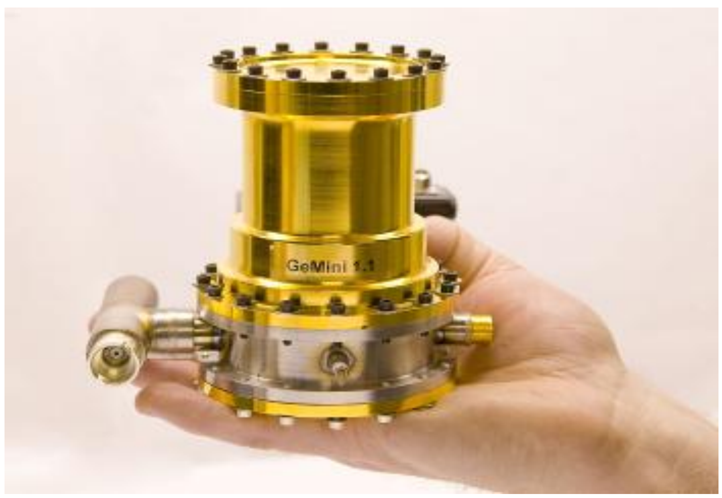

Figure 1 GeMini (<u>Ge</u>rmanium <u>Mini</u>ature spectrometer) has been designed to bring high-resolution gamma-ray spectroscopy to a range of demanding field environments. (2)

New detectors that may become suitable for safeguards in the future include Cadmium Zinc Telluride (CZT), Cadmium Manganese Telluride (CMT) and Cadmium Telluride (CdTe). Thallium Bromide (TlBr) (3) has achieved nearly 1% energy resolution, but it polarizes within a few days at room temperature which compromises charge transport, rendering it impractical at this time without some cooling (to -20^{0}C). Much prior research in Mercuric Iodide (3) has been conducted, but it still suffers from growth striations. The front-runners today are CZT and CMT, which routinely offer resolution of 2% or better at 662 keV for small crystals (<1cm^3). Improvements in size, thickness and resolution are needed for the CZT detector to become viable for Safeguards. Today, it is possible to grow larger volume single-crystals up to several cubic centimeters but they can include multiple domains (grain boundaries and twins), dislocations, and always have Te inclusions which adversely affect the mobility-lifetime product for electrons. Several companies are developing reproducible manufacturing processes to produce high yields and acceptable costs. CMT is promising alternative to CZT, where the energy resolution is ~4%, but the detector material is in very early stages of development but has perhaps the greatest potential to surpass the performance of CZT. The inherent advantage of CMT is the smaller percentage of Mn alloy required to attain the required bandgap. Disadvantages of CMT are that material specific fabrication processes need to be established and low purity manganese (3). While other semiconductors have in the past unsuccessfully challenged the CZT's dominance of room temperature operation (e.g. HgI_2), it appears that TlBr could become the front runner within a few years, as the "polarization problem" is becoming resolved.

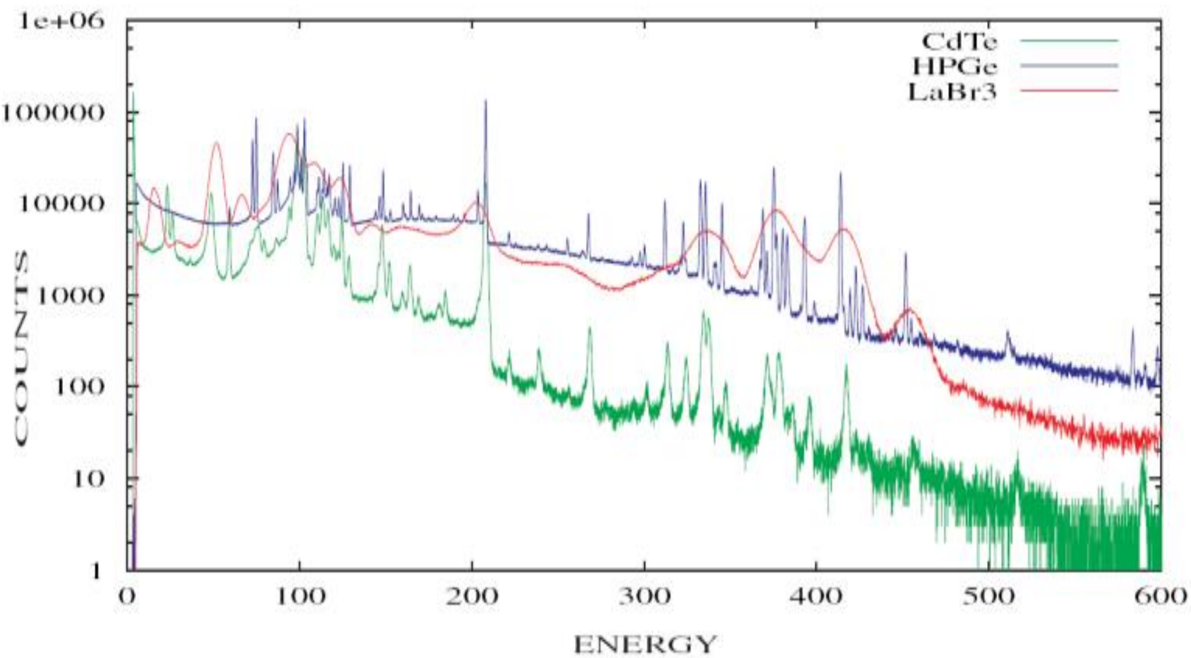

Figure 2 Comparison of energy resolution for high purity germanium, lanthanum bromide and cadmium telluride. (4)

Gamma Measurements of Enrichment

The measurement of uranium samples to establish the fraction of fissile ^{235}U is referred to as uranium enrichment. The term "enrichment" refers to the fact that the samples have more ^{235}U than is present in natural uranium. The technique is well established in the safeguards community. (Reilly, Ensslin, & Kreiner, 1991). The measurement requires an accurate measurement of the 186-keV peak of ^{235}U as well as the higher energy peaks of ^{238}U (1.064 MeV). Fig. 2 above contains a comparison of the spectra for several well-known materials.

Detectors used for enrichment measurements need to be rugged for factory environments, lightweight for handheld use. The detectors need to be able to be easily shipped. Temperatures range typically from -40 to +40C. In a product autoclave, temperatures can be -60C to 140C in both wet and dry conditions. A detector that performs without the use of cryogens, such as liquid nitrogen, is preferred. The measurements should be performed quickly.

- The detector currently used is Sodium Iodide (NaI) or CZT. NaI is limited by ruggedness and resolution. CZT is limited by efficiency and crystal size. Vo (5) performed a comparison of portable CZT, Lanthanum Bromide ($LaBr_{3)}$ and NaI detectors for enrichment measurements and concluded that overall $LaBr_3$ was preferable to NaI because of resolution and preferable to CdZnTe because of efficiency (see Fig. 2 above). Lanthanum halide single crystals are the highest performance spectroscopic gamma-ray scintillators with a higher light output per detected gamma, better energy resolution for spectroscopy, more proportional output, and room temperature operation. However, a disadvantage of $LaBr_3(Ce)$ is that it does not work well at autoclave temperatures and a better understanding of material mechanics is needed to increase material strength and toughness for use (6). The alternative mentioned with the highest TRL (9) was Cesium Iodide (CsI). Other alternatives suggested at the Workshop were Europium-doped Strontium Iodide [$SrI_2(Eu)$] (7), improved proportionality materials such as Elpasolites (6), and new scintillators such as $BaBr:Eu^{2+}$ (8) and certain transparent ceramics (7), see Figs. 3-5. Ceramics have several advantages over single crystals: unreactive with air and moisture, mechanically durable and high activator concentration & uniformity. Researchers so far have only obtained good energy resolution of nearly 4% for Garnets such as GYGAG(Ce). (7)

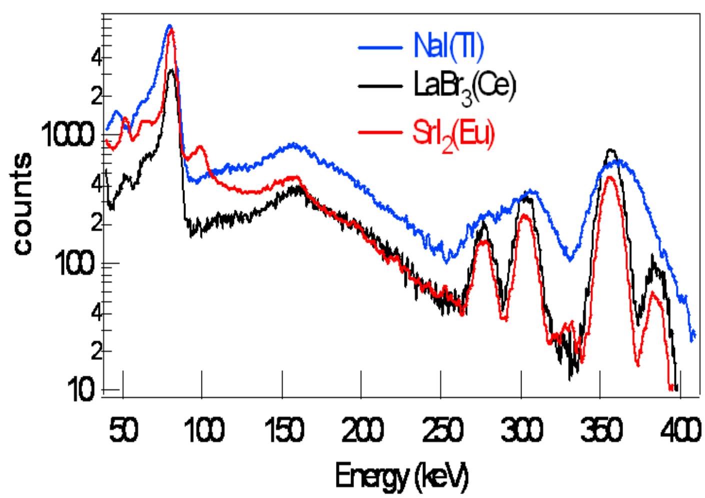

Figure 3 Comparison of energy resolution of three scintillators. LLNL expects to achieve <2.5% resolution at 662 keV with $SrI_2(Eu)$ by optimization. (7)

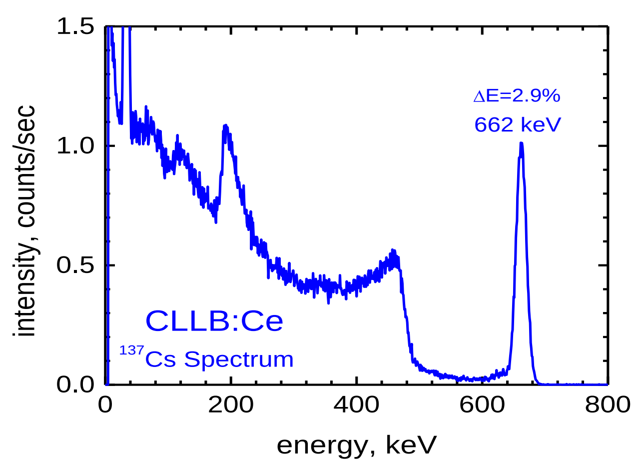

Figure 4 Gamma ray spectrum of ^{137}Cs with an Elpasolite crystal [$Cs2LiLaBr_6(Ce)$] (6)

Neutron Detection

Neutron detectors for safeguards are needed that are easy to operate, have a long mean time to failure, good discrimination between neutrons and gamma rays (i.e. insensitive to gamma-rays) and can be used for both thermal and fast neutron measurements. Ideally they would be inexpensive and readily available.

Helium-3 detectors are the workhorse for thermal neutron measurements. They have the advantage of being simple to operate, have excellent reliability, can tolerate high neutron fluxes without serious radiation damage and are insensitive to gamma-rays. The detectors can have good detection efficiency (Tubes of 2.5-cm diameter containing 4 atm of ^{3}He have an intrinsic detection efficiency of 90% for thermal neutrons.) Detector banks with these tubes placed 5 cm apart can be designed to have absolute detection efficiencies of about 20% for spontaneous fission neutrons (9).

<u>Total Neutron Counting or Coincidence Counting</u>

Detectors measuring neutron flux can be used for total neutron counting or coincidence counting. Examples of a total neutron counting instrument are a Shielded Neutron Assay Probe (SNAP detector), and a slab detector (9). The detectors are very simple moderated ^{3}He tubes. They are used to verify nuclear material such as uranium hexafluoride in enrichment facilities or plutonium metal, or to measure the holdup of nuclear material and verify the flow of nuclear materials.

A second use of neutron detectors is for coincidence counting. The principles of coincidence counting can be found in the PANDA manual (9). In general, neutron coincidence counters need higher detection efficiency than total neutron counting systems because of the requirement to count at least two simultaneous neutrons. Well counters or 4 pi counters are used because coincidence counting is proportional to the square of the detector efficiency. The main disadvantage of ^{3}He tubes for coincidence applications is that the neutrons must be thermalized before they are detected in the tubes and this causes a large die-away time in the detector. Neutron detectors for both applications require that they be quick, efficient, sufficiently large (e.g. to cover a canister), have at least a 10^5 discrimination of neutrons to gamma-rays, a short die-away time and be stable. Transportability is important, particularly for field instruments.

Many new neutron detectors are undergoing research at this time to substitute for ^{3}He detectors. A few candidates are available commercially, such as Boron Trifluoride (BF_3), which is also sensitive to thermal neutrons, but in general the detector must be shipped as hazardous material. The tubes are limited to lower pressures (0.6 atm) however it was noted that with improved engineering of the tubes or an alternative geometry such as wire chamber designs, this restriction may be lifted. Liquid scintillator is an alternative that is being considered and has the advantages of fast neutron detection. With nanosecond timing and pulse shape discrimination (see Figs. 6-7) it has been demonstrated to have good neutron to gamma separation (7). It is available commercially, however has limitations in high count rate environments and is flammable. New higher-flashpoint options are available (10). Molecular crystals such as Stillbene and fluoro-biphenyl lithium carboxylate (7) were mentioned. Stillbene is similar to liquid scintillators, in that they are sensitive to fast neutrons, 10^5 neutron to gamma discrimination and have a TRL~9. On the plus side, also, they are non-flammable. However, they are difficult to procure because of the way they are grown. LLNL has identified other crystalline scintillators (18) that have neutron-gamma separation similar to Stillbene; all of these organic compounds can be grown from solution to greatly reduce costs relative to conventional melt-growth.

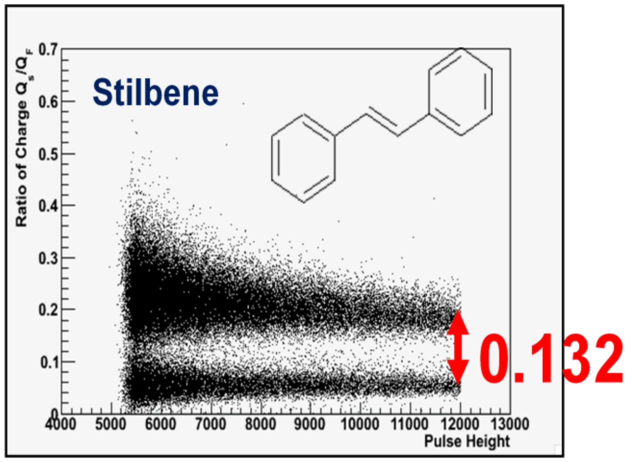

Figure 4 Neutron - gamma separation measured in Stillbene. (7)

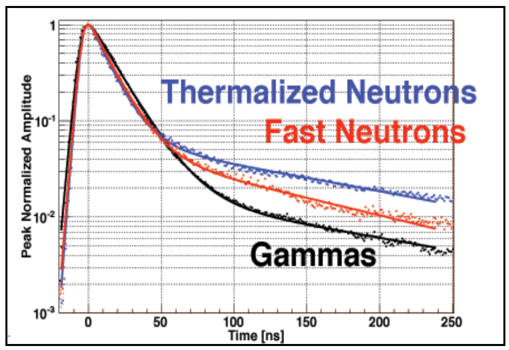

Figure 5 Certain organics (fluoro-biphenyl lithium carboxylate) detect both high-energy and thermal neutrons. (7)

Lithium-6 loaded glass scintillating fibers are commercially available as neutron detectors, but lack excellent neutron to gamma discrimination. Plastic scintillators can be loaded with boron and are commercially available for fast neutron detection. These have fast response times but are not used for safeguards because of their high gamma sensitivity. Other detectors include lithium-based scintillators, ranging from lithium glass plates (TRL 9) to Lithium Iodide (TRL 9) and CLYC [$Cs_2LiYCl_6(Ce)$] crystals. ^{6}Li glass detectors with improved gamma ray rejection (10^4 discrimination) are being developed by PNNL (11), Fig. 8. Previous experiments at the Savannah River National Laboratory demonstrated enhanced gamma-ray discrimination using an advanced Ce^{3+} doped ^{6}Li glass solid-state scintillator that offers efficient detection in a small package for neutron emitters while significantly reducing gamma-ray interferences. (12) All these need improved gamma rejection for use in safeguards.

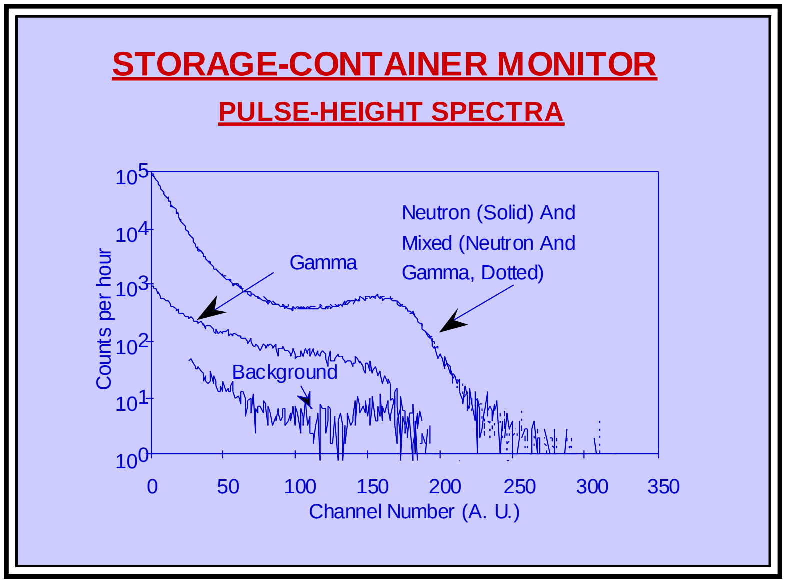

Figure 6 Pulse-height spectrum of Lithium-6 glass fibers showing improved gamma-ray rejection. (11)

Silicone rubber with boron loading was suggested as a novel detector, having the advantage of radiation resistance, and it can incorporate boron compounds easily utilizing carborane siloxanes for neutron detection. Loadings with 18% boron have been achieved at Oak Ridge National Laboratory. (13; 14). Cerenkov detectors were also mentioned. Semiconductors such as boron carbide, boron nitride (3), LiGaTe, LiZnN, etc. are in very early stages of development (TRL 1). A large monocrystal of $LiTaO_3$ looked promising as a large monocrystal if the traps can be improved.

Composite materials such as the Pillar Detector (7) rely on a carefully constructed platform of micron-size etched silicon pillars that are interspersed with ^{10}B, which converts incoming neutrons to alpha and lithium particles. The 3D structure maximizes the efficiency of the device. Incoming neutrons interact with the boron producing alpha and lithium particles that deposit their energy in the semiconductor and create the current that provides the electronic signal. Performance of the Pillar Detector once scaled should have the following figures-of-merit: efficiency >50 %, voltage <10V, neutron to gamma discrimination of $>10^5$, and fast timing to allow compatibility for multiplicity counting circuitry. They are currently made in small area; these could be tiled to create larger detectors. This work is related to the so-called “perforation detector” at Kansas State.

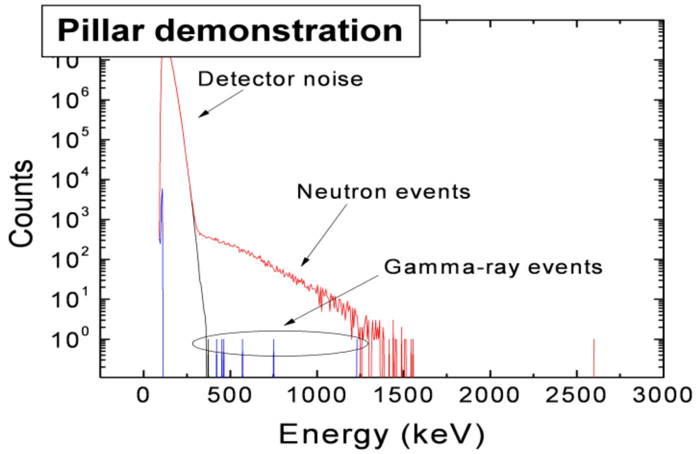

Figure 7 Demonstration of the use of a pillar detector to measure ^{252}Cf. (7)

Neutron Energy Measurements

Neutron detectors are also used to measure the neutron energy. This measurement can be used to determine the presence of oxide (helpful in coincidence counting analysis), as stationary detectors, to measure possible diversion and for measurements of spent fuel. The latter measurement requires detectors that can stand very high neutron and gamma ray fluxes. For neutron energy measurements, the detectors need to be simple to operate, have a long mean time to failure, good discrimination of neutrons from gamma rays, be inexpensive, available, can be sensitive to either thermal or fast neutrons. Currently a ring ratio multiplicity counter (9) is used to measure neutron energy as well as a series of Bonner Spheres, which is commercially available.

New methods discussed at the workshop were lithium fibers with moderators, liquid scintillator and PSD, organic crystals, a threshold detector, foil activation or double scatter techniques. Superconducting fast-neutron detectors (15) consist of a neutron absorber crystal and a thin film sensor operated at the transition between its superconducting and its normal state (transition edge sensor). Neutron capture in an (n, α) reaction deposits a total energy $E_{neutron} + Q_{(n,\alpha)}$, and the resulting temperature increase is measured in sensor resistance. Operation at very low temperatures reduces thermal noise and allows an energy-dependent energy resolution below 10 keV for fast neutrons in the MeV range. Prototype fast neutron spectrometers have been build based upon the ~mm^3 $TiBr_2$ or ~cm^3 enriched ^6LiF neutron absorbers coupled to superconducting Mo/Cu sensors. They are cooled to their operating temperatures around 0.1 K in an adiabatic demagnetization refrigerator. The TiB_2-based prototypes have achieved an energy resolution of 5.5 keV at a total energy of 2.9 MeV. The larger ^6LiF-based devices have achieved energy resolution below 50 KeV for MeV neutrons. They have efficiency above 1% for 1 MeV neutrons, and their response above $Q_{Li\text{-}6} = 4.78$ MeV is mostly set by the (n, α) absorption cross section in ^6Li.

Spent Fuel Measurements

Neutron detection in a spent fuel pool requires detectors that are rugged, small, lightweight and above stored assemblies. They need to be simple to operate, have a long mean time to failure, have good discrimination of neutrons and gamma-rays and be able to be used in a high neutron and gamma-flux. At times the water is cloudy, inhibiting vision for technologies using Cerenkov radiation methods. The array size and stacking configuration may limit access from above. For example, CANDU fuels use horizontally stacked.

Only gross defect measurements are used by the IAEA. To date, there is no partial defect tool in IAEA safeguards. The detector of choice is the Improved Cerenkov Viewing Device, ICVD. Factors for success include water quality, fuel assembly burnup, and residence time in the pool by the spent fuel (16). If this detector is not successful, he use of the Spent Fuel Attribute Tester (SFAT) and Irradiated Item Attribute Tester (IRAT) is attempted. CZT detectors are used because they are small and lightweight, and their resolution permits details in the gamma spectrum which can be used to assess qualitatively cooling time and burnup of spent fuel assemblies and to distinguish them from irradiated non-fuel items. A discussion of detectors for measuring spent fuel assemblies using CZT, see (17). A FORK detector is also used for measuring neutron and gamma-ray for attribute verification (consisting of an ionization chamber for measuring gammas and two fission chambers for measuring neutrons). It relies on information from the operator for verification. New materials that might be useful are silicon carbide, diamond or using a string of dosimeters.

Detectors for Harsh Environments

Examples of harsh environments for safeguards include acid and salt baths, the electrorefiner (high temperatures 450-500 C), product autoclave (low temperatures ~-60 C), and high radiation fields (spent fuel). The detectors must be ruggedized for the environment. In some cases that may mean they need to be waterproofed or there may be seismic requirements.

While not many specific technologies were mentioned other than engineering suggestions, a few suggestions were made in the workshop. A silica light pipe could be used for the detector such as is done in oil well gamma detectors for high temperature environments, and certain oxides such as GYGAG(Ce) might be viable. Cold temperatures may require encapsulation of the detectors. Scintillators and semiconductors seem to tolerate cold temperatures better than high temperatures.

NEXT STEPS

In the long term (longer than 3 years), researchers were encouraged to continue to look for new materials that have been discovered, could be engineered or made.

For the shorter term, new smaller mechanically cooled high purity germanium detectors offer an engineering solution for many safeguards needs for handheld high resolution detectors. CZT detectors with 0.5% resolution at 662 keV and 1% at 100 keV would be useful. High resolution from materials such as SrI_2(Eu) and CLLB(Ce) would be a better substitute for NaI(Tl) detectors used today. Substitutes for ^{3}He are needed now. An integrated look at the alternatives emphasizing performance for specific needs is warranted. Materials that might fill that need are the Pillar Detector, Stillbene, lithium-loaded glass fibers and liquid scintillators.

Safeguards researchers were encouraged to provide concrete applications and requirements to materials developers. Scenario “benchmarks” with specific requirements would be useful for performance testing. Materials developers would like more information about deficiencies and failures of current tools. A signatures and observables study to better understand specific detector needs for safeguards would be helpful.

ACKNOWLEDGEMENTS

The authors acknowledge the support of each individual participating in the Workshop and giving us input for this paper: Steve LaMontagne, Kevin Veal and David Beach, NNSA; Ralph James, BNL; Jeff Sanders and Mark Schanfein, INL; Steve Derenzo, Edith Bourett, Rob Johnson, LBNL; Zane Bell, John S. Neal, ORNL; Kiril Ianakiev and Debra Wrobleski, LANL; Tzu-Fang Wang and John Luke, LLNL; Michael Curtis, Kim Ferris, and Karl Pitts, PNNL; Patrick Doty, SNL; David Hanks and David Hathcock, SRNL. Special thanks are due to our Rapporteurs: Nerine Cherepy and Rebecca Nikolic. The authors wish to thank the United States National Nuclear Security Administration's Office of Dismantlement and Transparency for supporting this workshop. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

REFERENCES

1. *Next Generation Safeguards Initiative, NNSA Office of Nuclear Safeguards.*

2.Burks, M., "GeMini: The next-generation mechanically-cooled germanium spectrometer, " (2008) Nuclear Science Symposium Conference Record, IEEE .

3. James, R. B., "Advanced Radiation Detection Materials for Next-Generation Safeguards NDA," *Advanced Radiation Detection Materials for Safeguards NDA Meeting, June 2009.* Livermore, CA , 2009 and Hitomi, K. et al., "Improvement of energy resolutions in TlBr detectors," Nucl. Instrum. Meth. Phys. Res. A 607 (2009) 112–115.

4. Wang, T.-F., "Standard Testing Approaches for Nuclear Safeguards," *Advanced Radiation Detection Materials for Safeguards NDA Meeting, June 2009.* Livermore, CA , 2009.

5. Vo, D.T., "Comparison of Portable Detectors for Uranium Enrichment Measurements," J. of Radio. and Nucl. Chem., 276 (2008), 693-698.

6. Doty, F. P., "Advanced Radiation Detection Materials for Safeguards NDA", *Advanced Radiation Detection Materials for Safeguards NDA Meeting, June 2009.* Livermore, CA , 2009

7. Payne, S., Cherepy, N. and Nikolić, R., "LLNL Radiation Detector Materials Campaign", *Advanced Radiation Detection Materials for Safeguards NDA Meeting, June 2009.* Livermore, CA , 2009. N.J. Cherepy, et al., "Scintillators with Potential to Supersede Lanthanum Bromide", Submitted to IEEE Trans. Nucl. Sci., SORMA Proceedings issue. Nikolic, R. et al., "Pillar structured thermal neutron detector," 9th International Conference on Solid State and Integrated-Circuit Technology, 1-4(2008) 2353-2356.

8. Derenzo, S. and Bourret-Courchesne, E. "New Radiation Detector Materials," *Advanced Radiation Detection Materials for Safeguards NDA Meeting, June 2009.* Livermore, CA , 2009.

9. Reilly, D., Ensslin, N., Smith Jr., H. and Kreiner, S. *Passive Nondestructive Assay of Nuclear Materials.* Washington D.C. : U.S. Government Printing Office, 1991.

10. Eljen Technology Products. [Online] 2010. http://www.eljentechnology.com.

11. Pitts, W. K., "Advanced Materials for Safeguards Applications: PNNL Specialties." *Advanced Radiation Detection Materials for Safeguards NDA Meeting, June 2009.* Livermore, CA , 2009.

12. Hathcock, D. J., " Detector Materials Concepts for Safeguards Applications," *Advanced Radiation Detection Materials for Safeguards NDA Meeting, June 2009.* Livermore, CA , 2009.

13. Bell, Z. W., et al. "Detector Materials Research at ORNL," *Advanced Radiation Detection Materials for Safeguards NDA Meeting, June 2009.* Livermore, CA , 2009.

14. Bell, Z.M., "Boron-Loaded Silicone Rubber Scintillators," IEEE Trans. Nucl. Sc, 51(2004) 1773.

15. Hau, I.D., et al., "Neutron absorption spectroscopy for identification of light elements in actinides," Nucl. Instrum. Meth. Phys. Res. A 559 (2006) 745-747. and Niedermayr, T. et al., "Microcalorimeter design for fast -neutron spectroscopy," Nucl. Instrum. Meth. Phys. Res. A520 (2004) 70-72.

16. Boyer, B. "The Rudiments of IAEA Safeguards and an Introduction to the Key Role of the Inspector," Los Alamos National Laboratory, LA-UR 09-00207, 2010.

17. Arlt, R., Ivanov, V. and Parnham, K. "Advantages and Use of CdZnTe Detectors in Safeguards Measurements", [Online] http://www.evmicroelectronics.com/pdf/Applications/Advantages%20and%20use%20of%20CdZnTe.pdf.

18. Zaitseva N. P. et al., "Neutron detection with single crystal organic scintillators," Proc. of SPIE Vol. 7449 744911-7.